

HEAVY METAL CONTENTS IN MARINE SEDIMENTS AND SEAWATER AT TOTOK BAY AREA, NORTH SULAWESI

By :

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ABSTRACT

The study area is located in north-eastern part of Tomini Bay, approximately 80 km south of Manado city, North Sulawesi. This area is closed to submarine tailing disposal system in Buyat Bay.

Five marine sediment samples and four water samples from seawater and dig wells have been used for heavy metals (Hg, As, CN) analyses by using Atomic Absorption Spectrometry (AAS). This study is a part of research conducted by Marine Geological Institute on morphological changes of seabed in the Totok Bay. The result shows that concentration of mercury (Hg) in water samples taken from Rataotok estuary is higher than standards stipulated Government Regulation (Peraturan Pemerintah/PP) No. 82/2001. Meanwhile, concentration of arsenic (As) is almost reaching its standard threshold, and conversely cyanide (CN) concentration is low. This value of mercury (Hg) concentration taken from Rataotok estuary is much higher than water samples from of Buyat Bay estuary. Significant concentration of mercury (Hg) analysed from those particular sampling sites indicated high mercury contamination. Therefore, further examination on ground water of dig wells is necessary, especially for mercury analysis (Hg). Furthermore, comparing the formerly obtained data of mercury concentration in the sediment, this particular study concludes that the sediments in the Totok Bay had contaminated by mercury from gold-processing of illegal mining.

Keywords: pollution, heavy metal, marine sediment, seawater, Totok Bay

SARI

Daerah penelitian terletak di bagian timur laut Teluk Tomini, sekitar 80 km selatan kota Manado, Sulawesi Utara. Lokasi ini berdekatan dengan tempat pembuangan limbah tambang bawah laut di Teluk Buyat.

Lima contoh sedimen laut, lima buah contoh air dari laut dan sumur telah digunakan untuk analisa logam berat (Hg, As, dan CN) menggunakan metode Atomic Absorption Spectrometry AAS. Studi ini merupakan bagian dari penelitian yang dilakukan oleh Pusat Penelitian dan Pengembangan Geologi Kelautan tentang perubahan morfologi dasar laut di Teluk Totok. Hasil

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penelitian menunjukkan bahwa kandungan merkuri dalam contoh air yang diambil dari sekitar muara sungai Ratatotok lebih tinggi dari standar Peraturan Pemerintah/PP No. 82/2001. Sementara itu, konsentrasi arsen (*As*) hampir mencapai ambang batas standar dan konsentrasi sianida (*CN*) jauh lebih rendah dari standar ambang batas. Nilai kandungan merkuri di estuari Ratatotok lebih tinggi dibandingkan dengan contoh air yang terukur dari muara sungai di Teluk Buyat. Kandungan merkuri yang tinggi ini menunjukkan adanya indikasi pencemaran logam berat, dan oleh karena itu air di sumur-sumur penduduk perlu dilakukan penelitian lebih lanjut, khususnya untuk analisa merkuri. Selain itu, berdasarkan perbandingan kandungan merkuri dalam sedimen pada penelitian sebelumnya, dapat disimpulkan bahwa Teluk Totok telah mengalami kontaminasi merkuri dari penambangan emas ilegal.

Kata kunci: polusi, logam berat, sedimen laut, air laut, Teluk Totok

INTRODUCTION

The study area is located in northeastern part of the Tomini Bay, approximately 80 km south of Manado City, North Sulawesi (00°51'12"- 00°54'20"N and 124°41'00"- 124°45'00" E). This area can be represented as a bay territorial with an estuary of river which flows from the valley of Ratatotok hinterland (Figure 1).

An estuary is a semi-enclosed coastal body of water with one or more rivers or streams flowing into it, and connected to the open sea, hence most of estuaries are highly influenced by tidal waves and dominated by muddy substrate carried by either freshwater or seawater (Bengen, 2004). The estuary in Totok Bay could be described as an enclosed coastal environment surrounded by small islands, coral reefs, and a spread of vast landscape in front of the estuary, especially when the tide is receding. Most parts of the coastal area of the Totok Bay are affected by oceanic processes, such as tides and waves that cause erosion and sedimentation. Most of this coastal area is inhabited by fishermen, but ironically, it is also very vulnerable to pollution due to mismanagement of waste. In the south-western part of the Totok Bay, lies Buyat Bay, a location that has been used for submarine tailing disposal system. It was discharged on to the seabed off the Buyat Bay at a water depth of 82 m. This location was

famous due to health problem occurred in many local people and environmental issues. Therefore many studies have been done both by national and international researchers for finding out the cause of this problem.

Investigations conducted by WHO and Japan National Institute for Minamata Disease produced a fact that Totok Bay was more polluted than Buyat Bay (WHO, 2004). Commonwealth Scientific and Industrial Research Organization (CSIRO), another research institute, has showed a similar result (CSIRO, 2004) compared to both previously mentioned investigations. Despite the conclusion of those researches, another investigation conducted by Wahana Lingkungan Hidup (WALHI) had developed a complete distinct conclusion, which showed that mercury (Hg) concentration in regencial water of Buyat Bay was higher than in Totok Bay (Maimunah et al., 2004). This inconsistency had made the authors to write a report on further investigation conducted by Marine Geological Institute in the estuary of Ratatotok River.

Blackwood and Edinger (2006) studied the sediment samples from the Buyat and Ratatotok Bays which were carried out in 2002 and 2004 for mineral and trace element analyses. Their study shows that high concentrations on arsenic (590–660 ppm), antimony (490–580 ppm), and mercury

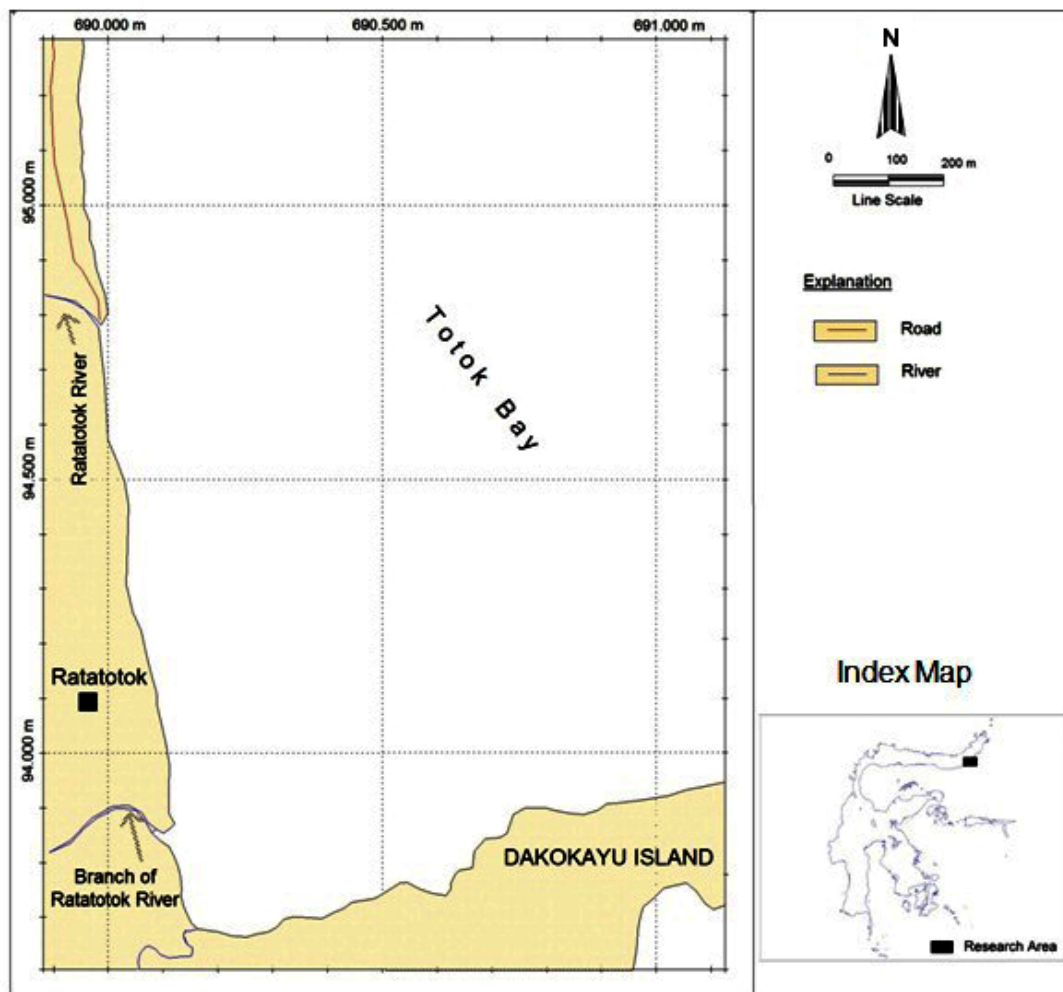


Figure 1. Study area (Ilahude et al, 2009)

(0.8–5.8 ppm) on shallow marine sediments of both Buyat and Totok Bay. Pre-mining, the concentration of arsenic concentrations in deep portions of Buyat Bay was range from 0 to 25 ppm (PT. NMR, 1994).

Furthermore, Endinger et al. (2006) characterized metal composition of mine tailings river sediments and marine sediments in the Buyat-Rataotok District. It shows that sediment affected by tailing has concentrations of As and Sb 20-30 times than in not contaminated sediments. Distribution of

mercury reaches up to 4 km from the river mouth.

Moreover, Edinger et al (2008) gave evidence that coral reefs in the Buyat Bay are affected by trace elements from the submarine disposal of tailings such as silicon, manganese iron, copper, chromium, cobalt, antimony, thallium, etc. All the above studies used both sediment and water samples that collected in 2002 and 2004. Therefore, the present study that collected samples in 2009 is in order to re-evaluate the level of heavy metals pollution

post-gold mining activities. Results of this study are expected to be a significant input for the local government to conduct a considerable action concerning the illegal mining activities (IMA) that contribute to waste disposal into Ratatotok River.

Problems caused by heavy metals waste produced by illegal mining need special awareness from related parties. Furthermore, this contamination of particular waste hypothetically occurred in the estuary near a former port of PT. NMR, which is now has been converted into a tourist destination beach. Based on details stated above, therefore the present study performs a series of sampling in

marine sediment in the estuary area of Ratatotok River, near-shore and fresh water from local dig wells.

Regional Geology

According to Efendi and Bawono (1997), lithology of study area are limestones, consists of coral reef limestone, sandy limestone, and clayey-limestone. Furthermore, the southern part of it consists of volcanic rocks, such as breccia, lava, and tuff, while the eastern part consists of lake and river sediments, consists of sand, silt, conglomerate, and marly clay. On the other hand, rocks in the coastal area is

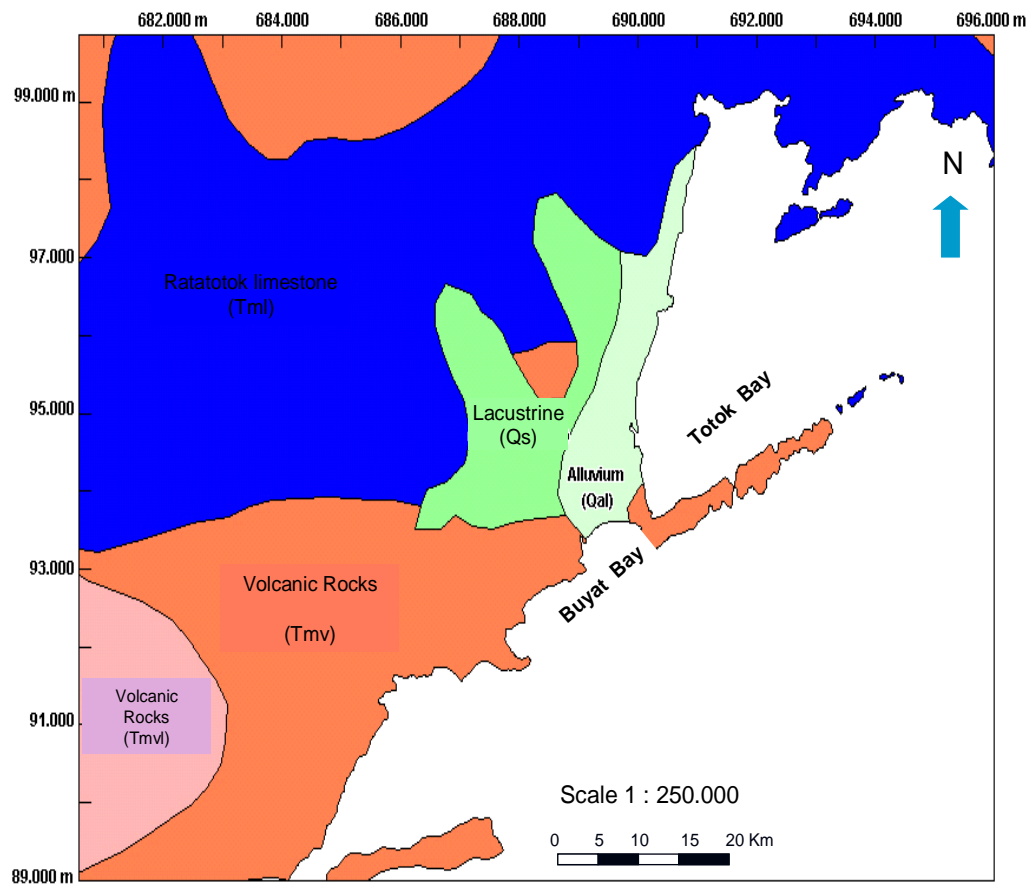


Figure 2. Geology of Manado Sheet (Efendi and Bawono, 1997)

composed by boulders, cobbles, pebbles, sand, and mud (Figure 2).

Gold bearing sedimentary rocks in the area are grey limestones, breccia limestones, and contacts between andesite and limestones such as calcite and quartz veins (Lahar, 2004). In above mentioned type of rocks, the prospectus of obtained gold ranged between 0.8 to 5 grams/ton. Processing of the gold ore was done in several ways as amalgamation, cyanidation, smelting, etc. The preference of gold processing depends on the condition of

the ore, namely the bond between the gold and the other minerals, the size of the granule, the hardness of the ore, and the mass of gold in the alloy itself.

According to Lahar (2001), cyanidation and amalgamation process are the most developing methods of gold processing. It was much attention from the government, regarding of their use of hazardous material and harmful compound which can cause environmental deffect. Generally, the environmental contamination is decreasing

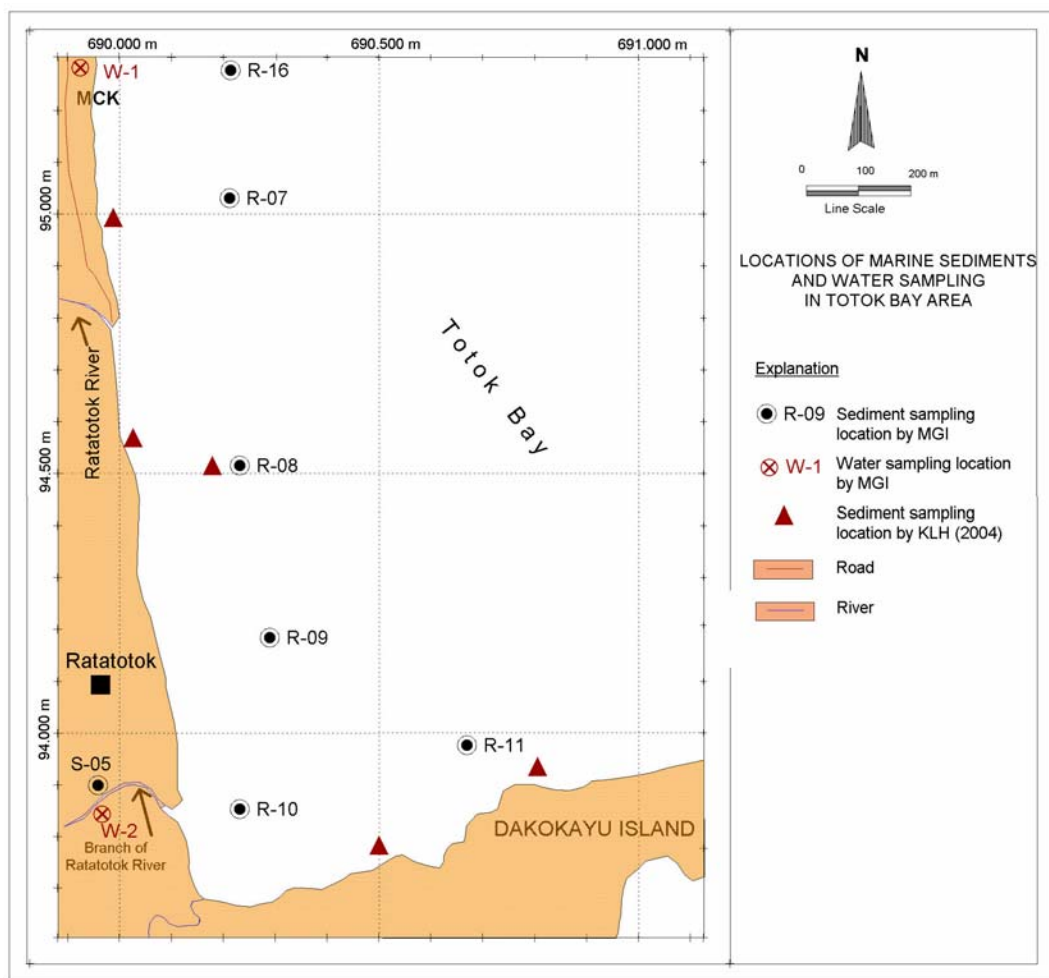


Figure 3. Location of marine sediment and water samplings in Totok Bay area. (Ilahude, et.al., 2009)

due to over limited mercury (Hg) used in public mining has not been well supervised by the government yet, since public awareness and mercury contamination control apparatus are absence.

METHODS

Five sediment and seven water samples were carried out in Totok Bay area. A grab sampler and Nansen bottle were used for these sampling (Figure 3). Some sediment samples were megascopically described, and the rest samples were appropriately stored to be further analyzed for heavy metals contents in the laboratory.

Preparation of grain size analysis in the laboratory was done by separation of the sediment granules based on its size through wet sieving system. After passed through a dehydration process to dry up the sediments, each sample was filtered from -2.0 phi to 4.0 phi fractions, and from 4.0 phi to 8.0 phi fractions. Data obtained from this process were analyzed using software to have the classification of the size of sediment granules such as sortation, skewness, and kurtosis. This categorization was re-processed using software to acquire the type of sediments classified in Folk (1980).

The heavy metals contents on sediments were analyzed using Atomic Absorption Spectrometry (AAS) in Quaternary Laboratory, Geological Research and Development Centre. Water samples, both from seawater and dig wells on land, were analyzed using Standard Methods for The Examination of Water and Wastewater (SMEWW). This method was acknowledged as an Indonesian National Standard, referred Ministerial Decree No. 51/2004 on seawater pollution standards, the same minimum safety standard as set by WHO.

RESULTS AND DISCUSSIONS

Sea Floor Sediments

In general, sediments covering the area of Totok Bay were dominated by fine fractions like silty sand and sandy silt. General characteristics of sandy silt are brownish yellow to dark grey coloured, and soft. While other types of sediments were coarse fractions such as sand deposits and silty sand with a small amount of gravelly components (Prihandono in Ilahude, et al., 2009). Based on data of megascopic analysis and a classification by Folk (1980) it is concluded that sediments of Totok Bay could be classified in to 3 types: sandy silt (sZ), silty sand (zS), and sand (S), as seen in the sediment distribution map of Totok Bay (Figure 4).

It showed that sediments with coarse granules covered the borderline of the study area, while the sediments with soft granules covered up the middle area toward the offshore area. The sediments with coarse granules were commonly accumulated in front of estuary, as found in front of Ratatotok River. Supply of sediments with such granules which occurred along the shorelines through the offshore was assumed to be altered by the energy of waves and tides originated from east and south-east directions.

Conversely, the sediments with finer granules were covering broader area than the other type of sediments. It is assumed as a result of mixture between fluvial and tidal processes, where the difference of water density would generate a certain pattern of tide in a narrow bay area, such as estuary of Ratatotok River.

Based on seafloor morphology (Figure 5), the middle part of this area was expanded to the ocean and tends to be shallowing. This morphology corresponded with the sediments supply from the land through the estuary of Ratatotok River. It was assumed that this

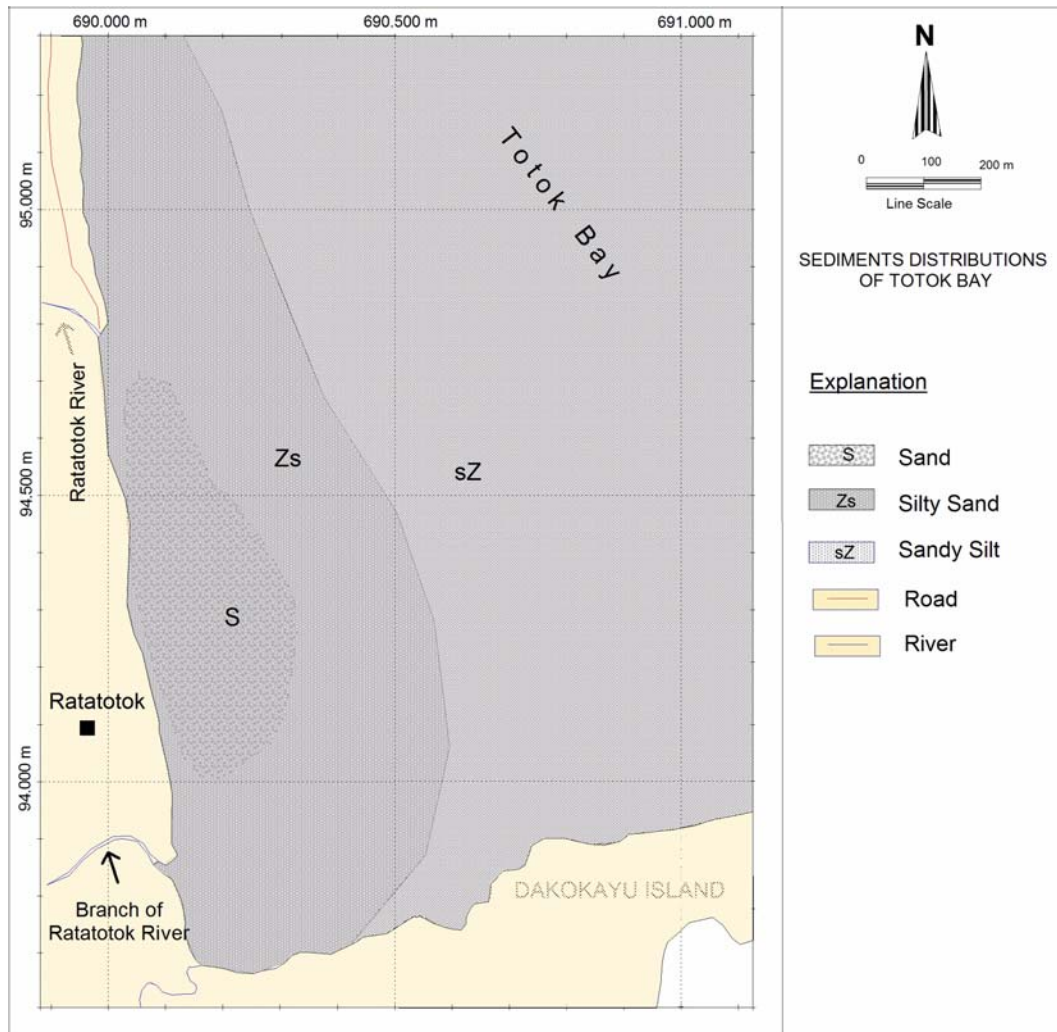


Figure 4. Surficial sediment distributions of the Totok Bay (Ilahude et al, 2009)

sediments supply from the estuary of this river contained heavy metals waste produced by illegal miner in Ratatotok. Concurrently, there were also heavy metals contaminations in the sediments of southern part of this research area, which assumed to be originated from the branch of Ratatotok River.

Mercury (Hg) and Arsenic Contents (As) in Water

Water samples were obtained from Totok Bay area. Moreover, we also used data of analyzed water samples from the Buyat Bay (Ilahude et al, 2009) as a correlative data required for further analysis. The results of these water analysis showed that the condition of mercury (Hg), arsenic (As) and cyanide (CN) from Ratatotok estuary are higher than

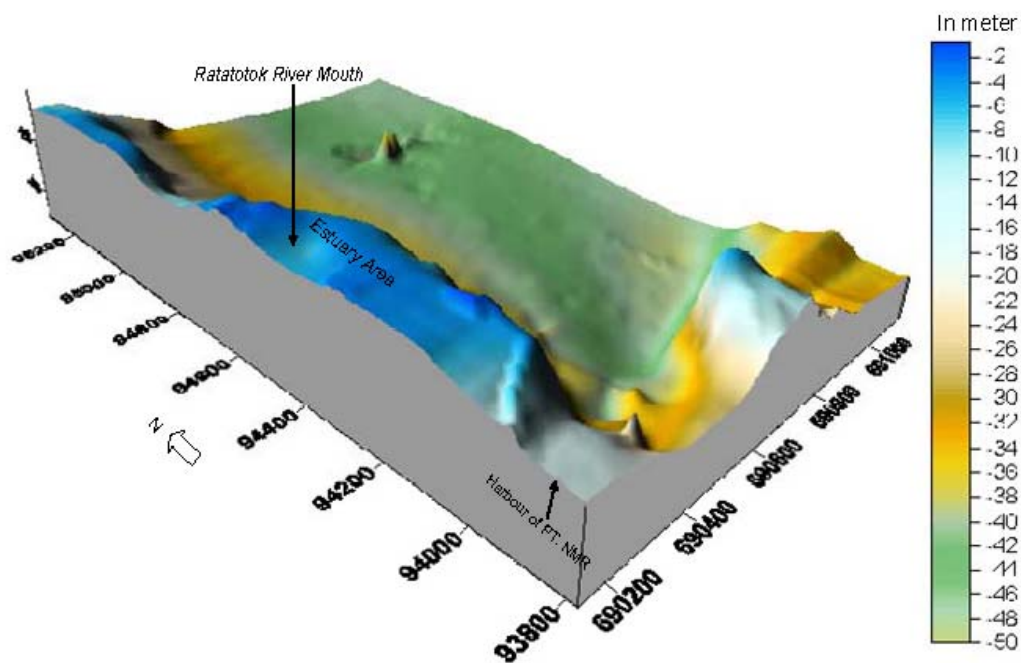


Figure 5. Seafloor morphology of the Totok Bay

Table 1. Heavy metal content in sea water and in public water reservoir/dig well

No.	Location	Water Quality Standards based on Government Regulation <i>No. 82 of 2001 (Class I)</i> in ppm			Water Samples Analysis (ppm)		
		Mercury (Hg)	Arsenic (As)	Cyanide (CN)	Mercury (Hg)	Arsenic (As)	Cyanide (CN)
1	Public Water Reservoir of Ratatotok (W-1)	0.002	0.05	0.02	0.06	0.043	0.003
2	Estuary of Lakban River in Ratatotok (W-2)	0.002	0.05	0.02	0.19	0.0005	0.003

Table 2. Heavy metal content in sea water of the Buyat Bay (Ilahude et al, 2009) and Water Quality Standard based on Government Regulation No. 82/2001- Class 1

No.	Heavy metal	Average (ppm)	Minimum (ppm)	Maximum (ppm)	Water Quality Standard
1	Hg	0.0600	0.0600	0.0600	0.002
2	As	0.0028	0.0002	0.0054	0.050
3	CN	0.0045	0.0040	0.0050	0.020

standards stipulated in Government Regulation (Peraturan Pemerintah/PP) No. 82 of 2001 (Table 1).

Concentrations of mercury (Hg) in water samples taken from the mouth of the river on the Lakban River is 0.19 ppm, while arsenic and cyanide are still below the specified quality standards. Unexpected results were found in this study that mercury (Hg) contamination occurred in one of the public dig well. A dig well in Ratatotok, serving as main water resources for bathing, washing, drinking and lavatory needs, had been examined and Hg content is 0.06 ppm. This value is above the threshold level of water quality standards specified in Government Regulation No. 82 of 2001 (Ariane in Ilahude, et al., 2009), while the content of arsenic (As) is almost reaching the threshold of water quality standard, except for cyanide (CN), which is still far below the quality standard limits (Table 1). This condition indicated that the contamination of mercury and arsenic waste derived from unauthorized gold processing of illegal miners (Penambangan Tanpa Izin - PETI) in public water reservoirs of Ratatotok. A significant concentration of mercury (Hg) indicated that the main source of mercury contamination had been caused by human activities, whereas for arsenic constituent, which was in close proximity to the threshold, should be re-evaluated (Herawati in Ilahude et al., 2009).

Conversely, the result of water samples analysis taken from the estuary and sea water in Buyat Bay, particularly on mercury (Hg) constituents, was above the quality standards specified in Government Regulation (Peraturan Pemerintah – PP.) No. 82, but was inversely lower than water samples taken at the estuary of Ratatotok River (Table 2). The amount of mercury detected in the estuary of Buyat River can be assumed as an outcome of illegal mining activities which throw its gold processing waste out into the river, in post-closure activities of PT. NMR in Ratatotok.

This condition was fairly different from investigation results acquired by an integrated research team of KLH in 2004 at Totok Bay and Buyat Bay prior to the cessation of PT. NMR. Five sea water samples were tested on the content of mercury (Hg), arsenic (As) and cyanide (CN). The result showed that the content of heavy metals constituents was relatively small and all of its value was below the water quality standards specified in Government Regulation No. 82 of 2001. Therefore, Buyat and Totok Bays were conclude had no heavy metals contamination at that moment of present study, as stated in Table 3 and 4.

Despite the results obtained, a research accomplished in June 2009 conducted by a research team of the Marine Geological Institute, we had also investigated the public water reservoirs (dig wells) and the estuary areas of Ratatotok coast. It was observed that

Table 3. Heavy metal content in sea water of the Buyat Bay (KLH, 2004) and Water Quality Standard based on Government Regulation No. 82/2001-Class 1

Amount of Sample (s)	Heavy Metal	Average (ppm)	Min. (ppm)	Max. (ppm)	Water Quality Standard
5	Hg	0.0005	0.0005	0.0005	0.0020
5	As	0.0094	0.0080	0.0110	0.0500
5	CN	0.0074	0.0040	0.0092	0.0200

Table 4. Heavy metal content in seawater of Totok Bay Sea (KLH, 2004) and WQS (Water Quality Standard based on Government Regulation No. 82/2001-Class 1)

Amount of Sample (s)	Parameter	Average (ppm)	Minimum (ppm)	Maximum (ppm)	Water Quality Standard
5	Hg	0.0005	0.0005	0.0005	0.0020
5	As	0.0042	0.0020	0.0070	0.0500
5	CN	0.0074	0.0054	0.0092	0.0200

Table 5. Heavy metal content in marine sediments (Ilahude et al, 2009)

Sample Code	Arsenic / As (ppm)	Mercury/Hg (ppm)
R - 07	21.0	6.367
R - 08	127.8	3.638
R - 09	9.3	4.126
R - 10	11.2	2.083
R - 11	20.0	3.420
R- 16	19.6	3.947

the mercury content was above the threshold level of water quality standards stipulated in Government Regulation No. 82 of 2001. This fact indicated an actual waste of illegal mining had occurred in particular location.

Mercury Content (Hg) in sediments

Gold-processing done by illegal miners yielded a huge mass of waste, including tailing remnants and minerals, which was all thrown out into the main river (Ratatotok River) and drained out into Totok Bay. As a consideration, Lahar (2001) stated that each gold-processing procedure would yield approximately 1.5% mercury (Hg), whereas the yield of other metals such as Cu, Pb and Zn was relatively low, excluding arsenic (As), which was between 4 to 130 ppm (Lahar, 2001), and 5 - 10 ppm mercury in sediments in the Ratatotok River (Edinger et al. 2007).

On the other hand, a study conducted by the MGI in 2009 had showed that concentrations of mercury was relatively high in the estuary area of Ratatotok River, as

valued 6.367 ppm at the point of R-07 (Table 5). The tested mercury level exceeded the standard set by Ministerial Decree No. 51/2004 on seawater pollution standard; value is higher than that analyzed by the integrated team from the Ministry of Environment (KLH) in the year 2004 in the exact similar location, which yielded in mercury concentrations in the range of 3 to 4.5 ppm.

Correspondingly, the value of mercury detected in Buyat Bay would still be higher than the tailings disposal site in Buyat Bay, which ranged from 0.88 to 1.16 ppm (KLH, 2004). Laboratory analysis result, shows that mercury content tend to increase pasca mining activities. Comparison of mercury concentration reported in pre-mining period (PT. NMR, 1994) with the later study conducted by Blackwood and Edinger (2007), it showed a similar trend of escalation whereas concentrations reported by PT. NMR (1994) increased between 0.8 and 5.8 ppm (Blackwood and Edinger, 2007) measured in industrial mine tailings in 2002 and 2004.

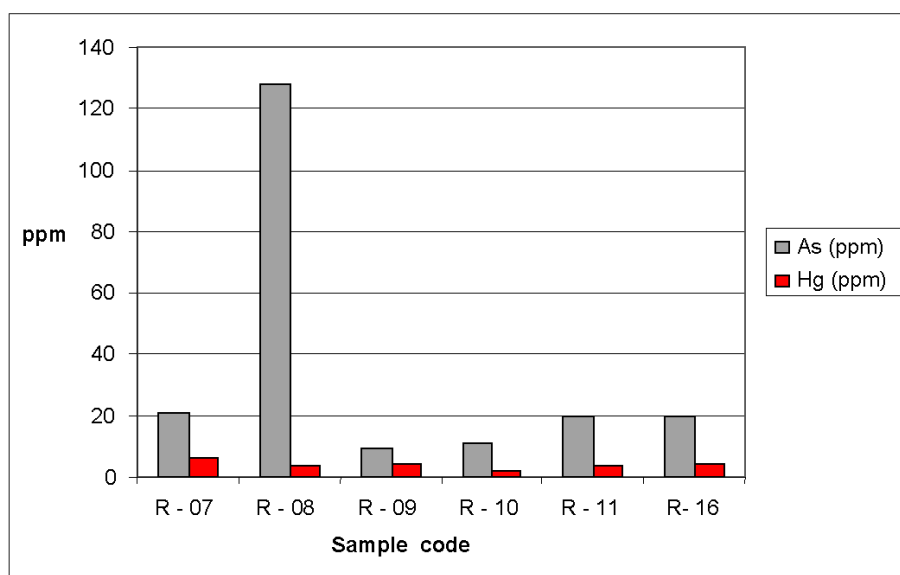


Figure 6. Diagram of heavy metals constituents in sediments samples in estuary areas of Ratatotok River

This particular study concludes that the sediments in the Totok Bay had encountered a mercury contamination from unauthorized gold-processing of illegal mining.

Concentrations of Arsenic (As) in Sediments

The highest concentration of arsenic in the sediment of Totok Bay, was found in the estuary area (R-08 = 127.8 ppm) and the lowest was found at the site R-09 is 9.3 ppm (Table 5). The highest value content of arsenic in the sediment in the estuary area, allegedly associated with the accumulation of arsenic waste disposal in the upstream of Ratatotok River which ranged from 4 to 130 ppm (Lahar, 2004). Arsenic sediment in the estuary of the Ratatotok River tends to shift toward the north as observed in the location of sample R-16. High content of arsenic is commonly found in the estuary area as seen in sediment samples R-10 and R-11 (Figure 3).

It was assumed that arsenic content in the sediment found in sites of R-10 and R-11 were part of arsenic waste disposal in the estuary of Ratatotok River. This suspicion was reconfirmed in the report done by the Ministry of Environment integrated team (2004). It stated that the illegal mining yielded waste of the amalgamation process had disposed into the tributaries in the upstream of Ratatotok River. Another confirmation of arsenic concentration escalation is obtained by comparing the pre-mining state reported by PT. NMR (1994) that ranged from 10 to 25 ppm which drastically increased to a range of 590-660 ppm, measured in samples of industrial mine tailings in 2002 and 2004 (Blackwood and Edinger, 2007). These previous results indicated that the waste disposal through the river to the sea caused by illegal mining had contributed to pollute the Totok Bay.

CONCLUSIONS

Sediment materials supplied through the mouth of the Ratatotok River allegedly contained mercury and arsenic (As) waste. Mercury constituents were assumed to be originated from the illegal mining activities in Ratatotok. The accumulation of mercury and arsenic in the estuary area of Ratatotok occurred during the gold mining activities.

The mercury content in water samples of public dig wells in Ratatotok was above the water quality standards stipulated in the Government Regulation No. 82 of 2001. This condition is very dangerous for people who consume water from those locations. Conversely, mercury, arsenic and cyanide in sea water samples were below the water quality standards, hence Totok Bay waters is safe as a habitat for marine biota.

To avoid further contamination of heavy metals waste which can cause severe health problems for the local peoples, it is advisable to do further research on the dig wells or water reservoirs in the estuary area of Ratatotok, regarding to the fact of excessive arsenic and mercury at the mouth of the Ratatotok River.

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